Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

THE DETERMINATION OF MAJOR ELEMENTS IN THE ASH OF SOLID MINERAL FUELS (CLASSICAL AND INSTRUMENTAL METHODS)

R. Prokopuk, L.C. Janke and W.J. Montgomery

Revised draft of TC 27 N1341

This document [illegible] is an [illegible] report [illegible] and [illegible] for discussion [illegible] reporting purposes [illegible] represent a final exp[illegible] the opinion of the [illegible] for Mineral and Energy Technology (CANMET)

Ce document [illegible] est un rapport [illegible] et [illegible] rédigé [illegible] de [illegible] documentation [illegible] mais [illegible] ne [illegible] décisive de [illegible] canadien de [illegible] minéraux et de [illegible] (CANMET)

36 pp

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 83-36(TR)

MAR 14 1994

MICROMEDIA

CONTENTS

	Page
1.0 SCOPE AND FIELD OF APPLICATION	1
2.0 REFERENCES	1
3.0 SUMMARY OF METHODS	2
3.1 General	2
3.2 Aluminum	2
3.3 Calcium	2
3.4 Iron	2
3.5 Magnesium	3
3.6 Potassium	3
3.6.1 Flame Photometric Method	3
3.6.2 Atomic Absorption Method	3
3.7 Silicon	3
3.8 Sodium	3
3.8.1 Flame Photometric Method	3
3.8.2 Atomic Absorption Method	4
3.9 Sulphur	4
3.10 Titanium	4
4.0 APPARATUS	4
4.1 Furnaces	4
4.2 Crucible and Lids	4
4.3 Spectrophotometer	4
4.4 Spectrometer	5
4.5 Hydrogen Ion Meter	5
4.6 Hotplate	5
4.7 Steam Bath	5
4.8 Glassware	5
4.9 Storage Bottles	6
4.10 Filter Paper	6
5.0 REAGENTS	6

Contents (Cont'd)

	Page
5.1 General	6
5.2 Preparation of Reagents	6
6.0 SAMPLE PREPARATION	13
6.1 General	13
6.2 Loss on Mass Heating	13
6.2.1 Procedure	13
6.2.2 Calculation	14
7.0 PROCEDURE	14
7.1 General	14
7.2 Control Blank	14
7.3 Quality Control	14
7.4 Elemental Analysis	14
7.4.1 Aluminum	14
7.4.2 Calcium	16
7.4.3 Iron	18
7.4.4 Magnesium	20
7.4.5 Potassium	20
7.4.5.1 Flame Photometric Method	20
7.4.5.2 Atomic Absorption Spectrophotometric Method	21
7.4.6 Silicon	22
7.4.7 Sodium	23
7.4.7.1 Flame Photometric Method	23
7.4.7.2 Atomic Absorption Spectrophotometric Method	24
7.4.8 Sulphur	24
7.4.9 Titanium	25
8.0 CALCULATION AND EXPRESSION OF RESULTS	26
8.1 General	26
8.2 Aluminum	27
8.3 Calcium	27
8.4 Iron	27

Contents (Cont'd)

		Page
8.5	Magnesium	28
8.6	Potassium	28
8.7	Silicon	29
8.8	Sodium	29
8.9	Sulphur	30
8.10	Titanium	30
9.0	PRECISION	31
9.1	General	31
9.2	Repeatability	31
9.3	Reproducibility	31
10.0	ANALYSIS REPORT	32

TABLES

No.		
1.	Concentration Ranges	1
2.	Spectrophotoscopy	5
3.	Reagent Table	9
4.	Dilution Table (for aluminum)	15
5.	Precision Limits	32

1.0 SCOPE AND FIELD OF APPLICATION

This proposal specifies the procedure for the elemental analysis of nine major constituents in ash, derived from either solid mineral fuels or semicoke and coke residues, obtained from Brown coals and lignites.

Table 1 identifies elements of interest and the procedure's applicable concentration range (note 1).

Table 1 - Concentration ranges

Element	Reported as oxide	Range per cent
Aluminum	Al_2O_3	12 - 30
Calcium	CaO	1.0 - 18
Iron	Fe_2O_3	2.0 - 40
Magnesium	MgO	0.4 - 4.5
Potassium	K_2O	0.2 - 2.0
Silicon	SiO_2	30 - 65
Sodium	Na_2O	0.1 - 3.0
Sulphur	SO_3	1.0 - 16
Titanium	TiO_2	0.5 - 2.0

Note 1 Phosphorous exists in ashes and may be determined (as P_2O_5) using ISO TC 27N 622 and included in material balance, when reporting.

2.0 REFERENCES

ISO 1988 Hard Coal Sampling

ISO 1171 Solid Mineral Fuels - The Determination of Ash

ISO 622 Solid Mineral Fuels - The Determination of Phosphorous

ISO 5725 Precision of Test Methods - Determination of Repeatability and Reproducibility by Interlaboratory Tests

1.0 SCOPE AND FIELD OF APPLICATION

This proposal specifies the procedure for the elemental analysis of nine major constituents in ash, derived from either solid mineral fuels or semicoke and coke residues, obtained from Brown coals and lignites.

Table 1 identifies elements of interest and the procedure's applicable concentration range (note 1).

Table 1 - Concentration ranges

Element	Reported as oxide	Range per cent
Aluminum	Al_2O_3	12 - 30
Calcium	CaO	1.0 - 18
Iron	Fe_2O_3	2.0 - 40
Magnesium	MgO	0.4 - 4.5
Potassium	K_2O	0.2 - 2.0
Silicon	SiO_2	30 - 65
Sodium	Na_2O	0.1 - 3.0
Sulphur	SO_3	1.0 - 16
Titanium	TiO_2	0.5 - 2.0

Note 1 Phosphorous exists in ashes and may be determined (as P_2O_5) using ISO TC 27N 622 and included in material balance, when reporting.

2.0 REFERENCES

ISO 1988 Hard Coal Sampling

ISO 1171 Solid Mineral Fuels - The Determination of Ash

ISO 622 Solid Mineral Fuels - The Determination of Phosphorous

ISO 5725 Precision of Test Methods - Determination of Repeatability and Reproducibility by Interlaboratory Tests

3.0 SUMMARY OF METHODS

3.1 General

Ash, prepared in accordance with ISO 1171 and ground in an agate mortar to pass a 0.063 mm square mesh test sieve, is subjected to the following methodologies:

3.2 Aluminum

A test portion is digested with hydrofluoric, nitric and sulfuric acids. The residue is fused with potassium or sodium pyrosulfate and the melt redissolved in hydrochloric acid. The pH is adjusted with acetic acid and ammonia. The solution is extracted with sodium diethyldithiocarbamate and chloroform. Aluminum is complexed with an excess of disodium ethylenediaminetetraacetate (EDTA) and determined indirectly by titrating the excess EDTA with standardized zinc solution.

3.3 Calcium

A test portion is fused with sodium carbonate and the melt redissolved in hydrochloric acid. The solution is fumed with perchloric acid and the resulting residue is filtered off, the filtrate being reserved (Solution A).

The insoluble residue is digested with sulfuric and hydrofluoric acids to remove silica and then fused with sodium pyrosulfate. This melt is redissolved in hydrochloric acid (Solution B), and combined quantitatively with the evaporate of Solution A to give Solution C.

The hydroxidic interferences in Solution C are precipitated with ammonia and filtered off. The filtrate is collected (Solution D). An aliquot of solution D is pH adjusted with sodium hydroxide to precipitate magnesium hydroxide. The solution is then titrated with standardized EDTA using NN indicator.

3.4 Iron

A test portion is digested with hydrofluoric, nitric and sulfuric acids. The residue is fused with potassium or sodium pyrosulfate and the melt redissolved in hydrochloric acid. The solution, pH adjusted with ammonia to precipitate ferric hydroxide is filtered. The recovered residue is redissolved in hydrochloric acid. Stannous chloride and mercuric chloride

are added. The iron content is determined by titration with standardized potassium dichromate, using sodium diphenylamine sulfonate indicator.

3.5 Magnesium

An aliquot of Solution D (3.3) is pH adjusted with ammonia. The interferences are complexed with cyanide solution and the solution is then titrated with standardized EDTA using EBT indicator.

3.6 Potassium

3.6.1 Flame Photometric Method

A test portion is digested with hydrochloric, hydrofluoric and perchloric acids. The salts are redissolved in hydrochloric acid and extracted with methylisobutylketone. The solution's pH is adjusted with ammonia and the interferences are complexed with the addition of ammonium oxlate. The solution is filtered and the potassium content in the filtrate is determined using a flame photometric technique.

3.6.2 Atomic Absorption Method

A test portion is digested with hydrochloric, hydrofluoric and perchloric acids. The precipitated salts are redissolved in perchloric acid. The potassium content in this solution is determined using an atomic absorption spectrophotometric technique.

3.7 Silicon

A test portion is fused with sodium carbonate and the melt redissolved in hydrochloric acid. The solution is fumed with perchloric acid (to dehydrate the silicon) and then filtered. Residual silicon in the filtrate is recovered by refuming with perchloric acid. The impure siliceous precipitates are combined, ignited and weighed. The ignited residue is then redigested with sulfuric and hydrofluoric acids, reignited and reweighed. The silicon content is determined gravimetrically from the difference in the two weighings.

3.8 Sodium

3.8.1 Flame Photometric Method

The sodium content in an aliquot from solution (3.6.1) is determined using a flame photometric technique.

3.8.2 Atomic Absorption Method

The sodium content in an aliquot from solution (3.6.2) is determined using an atomic absorption spectrophotometric technique.

3.9 Sulphur

A test portion is digested with hydrochloric acid. The pH of the filtrate is adjusted with ammonia. Addition of barium chloride precipitates the sulphur (as a sulfate) which is subsequently filtered, dried and weighed.

3.10 Titanium

A test portion is fused with sodium peroxide and the melt redissolved in hydrochloric acid. The ferric ion is reduced and subsequently complexed with ascorbic acid. The solution's pH is then adjusted. Titanium is complexed with diantipyrylmethane and the spectrometric absorbance of this solution is measured.

4.0 APPARATUS

4.1 Furnaces

4.1.1 Ashing furnace as specified in ISO 1171

4.1.2 Fusion furnace with an operating range of at least 1050 ± 50 degrees centigrade.

4.2 Crucible and Lids

Crucible and lids for fusion of the ashes shall be made of either pure platinum, platinum/gold alloy (95/5) or sintered alumina with capacities of at least 80 mL.

4.3 Spectrophotometer (Atomic Absorption or Flame Photometric)

The instrument should be equipped with interchangeable air-acetylene and oxy-hydrogen flame burners and either absorbance or direct concentration readouts. The fuel gas composition and wavelengths listed in Table 2 are recommended. Other instrument parameters shall be optimized in accordance with manufacturer's specifications, when operated.

Table 2 - Spectrophotoscopy

Element	Wavelength nm	Fuel Composition	Comments
Potassium	766.5	Oxy-hydrogen	Flame photometric mode
	766.5	Air-acetylene	Atomic absorption mode
Sodium	589.0	Oxy-hydrogen	Flame photometric mode
	589.0	Air-acetylene	Atomic absorption mode

4.4 Spectrometer

The instrument should be equipped with at least a 10 mm measuring cell with variable wavelength selection from 250 to 800 nanometers. Other instrument parameters shall be optimized in accordance with manufacturer's specifications, when operated.

4.5 Hydrogen Ion Meter

4.6 Hotplate

A hotplate with an operating range to 500 degrees centigrade and magnetic stirring capabilities is recommended; or a sand bath.

4.7 Steam Bath

4.8 Glassware

Grade A glassware shall be used unless otherwise specified (Note 3).

4.9 Storage Bottles

Bottles composed of glass (brown), polyethylene or polypropylene with screw caps and air-tight seals are recommended for solution storage (Note 3).

4.10 Filter Paper

Ashless, closed and medium textured, are recommended.

Note 3 All bottles and glassware shall be conditioned by presoaking in dilute nitric acid (1+19) for at least 24 h prior to use.

5.0 REAGENTS

5.1 General

Chemicals of analytical grade purity conforming to national standards shall be used in all tests.

5.2 Preparation of Reagents

Table 3 itemizes solutions required for element of interest.

5.2.1 Acetic acid (p_{20} 1054 kg per m^3)

5.2.2 Acetic acid (p_{20} 1054 kg per m^3), diluted 1+1

5.2.3 Acetone (p_{20} 794 kg per m^3)

5.2.4 Acetylene gas (compressed)

5.2.5 Acid mixture (binary)

Mix 150 mL of sulphuric acid (5.2.54) with 500 mL of water (5.2.59). Add 150 mL of phosphoric acid (5.2.37), cool to ambient and dilute to 1 L mark with water (5.2.59).

5.2.6 Ammonium chloride solution

Dissolve 10.000 ± 0.001 g of ammonium chloride (5.1) in 450 mL of water (5.2.59). Add a few drops of methyl red solution (5.2.32) and adjust the pH to 7.0 ± 0.2 (slightly alkaline) with ammonia solution (5.2.9). Dilute to the 500 mL volumetric mark with water (5.2.59).

5.2.7 Ammonium oxalate solution

Dissolve 30.00 ± 0.01 g of ammonium oxalate monohydrate (5.1) in 1 L of water (5.2.59). Stir vigorously. Filter the saturated solution before storage if it is not clear.

5.2.8 Ammonia (p_{20} 900 kg per m^3)

5.2.9 Ammonia (p_{20} 900 kg per m^3), diluted 1+1

5.2.10 Ascorbic acid solution

Dissolve 10.00 ± 0.01 g of ascorbic acid (5.1) in 1 L of water (5.2.59). The solution should be prepared fresh daily.

5.2.11 Barium chloride solution

Dissolve 85.00 ± 0.01 g of predried barium chloride (5.1) in 1 L of water (5.2.59).

5.2.12 Chloroform (p_{20} 1439 kg per m^3)

5.2.13 Compressed air

5.2.14 Diantipyrylmethane solution

Dissolve 15.00 ± 0.01 g of diantipyrylmethane (5.1) in 300 mL of water (5.2.59). Add 30 mL of sulphuric acid (5.2.54). Dilute to the 1 L volumetric mark with water (5.2.59). If necessary, filter before storing in a brown bottle.

5.2.15 Disodium ethylenediaminetetraacetate (EDTA) solution

Weigh 3.750 ± 0.001 g of EDTA (5.1) into a 1 L volumetric flask. Dilute to the mark with water (5.2.59). Standardize molality against zinc titrant (5.2.61) by pipetting 25 mL of EDTA solution (5.2.15) into a 300 mL beaker. Add 10.0 mL of ammonia solution (5.2.9), 50 mL of water (5.2.59) and adjust pH to 6.0 ± 0.2 with ammonia solution (5.2.9). Add a few drops of xylenol orange solution (5.2.60) and titrate to a pale pink endpoint with zinc titrant (5.2.61). Record volume used and calculate concentration factor (f) using:

$$f = \frac{V_2}{V_1}$$

where

f - the concentration factor for a 0.01 M EDTA solution (5.2.15)

V_2 - the volume of the Zinc titrant (5.2.61) used, mL.

V_1 - the volume of EDTA solution (5.2.15) used, mL.

5.2.16 EBT solution

Dissolve 0.200 ± 0.001 g of sodium 1 - (1 - hydroxy -2- napthlazo) - 6 - nitro -3- napthol -4- sulfonate (5.1) in 15 mL of triethanolamine (5.2.58) and 5 mL of ethanol (5.2.17).

5.2.17 Ethanol (p_{20} 793 kg per m^3), 95+5

5.2.18 Ferrous ammonium sulphate solution

Dissolve 13.00 ± 0.01 g of ferrous ammonium sulphate hexahydrate (5.1) in 700 mL of water (5.2.59). Add 30 mL of sulphuric acid (5.2.54). Cool solution to ambient and dilute to 1 L volumetric mark with water (5.2.59).

5.2.19 Hydrochloric acid (p_{20} 1190 kg per m^3)

5.2.20 Hydrochloric acid (p_{20} 1190 kg per m^3), diluted 10+6

5.2.21 Hydrochloric acid (p_{20} 1190 kg per m^3), diluted 1+1

5.2.22 Hydrochloric acid (p_{20} 1190 kg per m^3), diluted 1+3

5.2.23 Hydrochloric acid (p_{20} 1190 kg per m^3), diluted 1+4

5.2.24 Hydrochloric acid (p_{20} 1190 kg per m^3), diluted 1+9

5.2.25 Hydrochloric acid (p_{20} 1190 kg per m^3), diluted 1+10

5.2.26 Hydrofluoric acid (40% strength)

5.2.27 Hydrogen gas (compressed)

5.2.28 Hydrogen peroxide (30% strength)

5.2.29 Mercuric chloride solution

Dissolve 0.50 ± 0.01 g of mercuric chloride (5.1) in 90 mL of water (5.2.59). Dilute to the 100 mL volumetric mark with water (5.2.59).

5.2.30 Methyl isobutyl ketone (p_{20} 810 kg per m^3)

5.2.31 Methyl orange solution

Dissolve 1.00 ± 0.01 g of methyl orange (5.1) in 1 L of water (5.2.59).

5.2.32 Methyl red solution

Dissolve 0.200 ± 0.001 g of methyl red (5.1) in 90 mL of ethanol (5.2.17). Dilute to the 100 mL volumetric mark with water (5.2.59).

5.2.33 Nitric acid (p_{20} 1420 kg per m^3)

5.2.34 NN indicator

Mix 0.100 ± 0.001 g of ground 1- (2 hydroxy -4- sulfo-1-nathylazo) -2- hydroxy -3- napthoic acid with 10.00 ± 0.01 g of potassium nitrate (5.2.41).

5.2.35 Oxygen gas (compressed)

5.2.36 Perchloric acid (70-72% strength)

5.2.37 Phosphoric acid (p_{20} 1077 kg per m^3)

5.2.38 Potassium chloride (powder or crystals)

5.2.39 Potassium cyanide solution

Table 3 - Reagent table

REAGENTS		ELEMENT AS OXIDE								
		Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SiO_2	Na_2O	SO_3	TiO_2
Acetic acid (concentrated)	5.2.1	X								
Acetic acid solution (1+1)	5.2.2	X								
Acetone	5.2.3	X								
Acetylene gas (compressed)	5.2.4					X		X		
Acid mixture (binary)	5.2.5			X						
Ammonium chloride solution	5.2.6		X	X	X					
Ammonium oxalate solution	5.2.7					X		X		
Ammonia (concentrated)	5.2.8	X	X	X	X	X		X	X	
Ammonia solution (1+1)	5.2.9	X	X	X	X	X		X	X	
Ascorbic acid solution	5.2.10									X
Barium chloride solution	5.2.11								X	
Chloroform	5.2.12	X								
Compressed air	5.2.13					X		X		
Diantipyrylmethane solution	5.2.14									X
Disodium ethylenediaminetetraacetate solution	5.2.15	X	X		X					
EBT solution	5.2.16				X					
Ethanol (95+5)	5.2.17		X	X	X					
Ferrous ammonium sulfate solution	5.2.18			X						
Hydrochloric acid (concentrated)	5.2.19	X	X	X	X	X	X	X	X	X
Hydrochloric acid solution (10+6)	5.2.20					X		X		
Hydrochloric acid solution (1+1)	5.2.21	X				X		X		X
Hydrochloric acid solution (1+3)	5.2.22			X					X	X
Hydrochloric acid solution (1+4)	5.2.23		X		X		X			
Hydrochloric acid solution (1+9)	5.2.24	X		X						
Hydrochloric acid solution (1+10)	5.2.25		X		X		X			
Hydrofluoric acid (40%)	5.2.26	X	X	X	X	X	X	X		
Hydrogen gas (compressed)	5.2.27					X		X		
Hydrogen peroxide (30%)	5.2.28									X
Mercuric chloride solution	5.2.29			X						
Methyl isobutyl ketone	5.2.30					X		X		
Methyl orange solution	5.2.31								X	
Methyl red solution	5.2.32		X	X	X					
Nitric acid	5.2.33	X		X		X		X		
NN indicator	5.2.34		X		X					

Table 3 - Cont'd

REAGENTS		ELEMENT AS OXIDE								
		Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SiO_2	Na_2O	SO_3	TiO_2
Oxygen gas (compressed)	5.2.35					X		X		
Perchloric acid (concentrated)	5.2.36		X		X	X	X	X		
Phosphoric acid (concentrated)	5.2.37		X							
Potassium chloride	5.2.38					X				
Potassium cyanide solution	5.2.39		X		X					
Potassium dichromate solution	5.2.40			X						
Potassium nitrate	5.2.41				X					
Potassium standard solution	5.2.42					X				
Silver nitrate solution	5.2.43								X	
Sodium carbonate	5.2.44		X		X		X			
Sodium chloride	5.2.45							X		
Sodium diethyldithiocarbamate solution	5.2.46	X	X		X					
Sodium diphenylamine sulfonate solution	5.2.47			X						
Sodium hydroxide solution	5.2.48		X		X					
Sodium peroxide	5.2.49									X
Sodium pyrosulfate	5.2.50	X	X	X	X					X
Sodium standard solution	5.2.51							X		
Stannous chloride solution	5.2.52			X						
Sulphuric acid (concentrated)	5.2.53	X	X	X	X		X			
Sulphuric acid solution (1+1)	5.2.54	X	X	X	X		X			X
Sulphuric acid solution (1+9)	5.2.55									X
Tin metal granular	5.2.56			X						
Titanium standard solution	5.2.57									X
Triethanolamine	5.2.58				X					
Water (distilled)	5.2.59	X	X	X	X	X	X	X	X	X
Xylenol orange solution	5.2.60	X								
Zinc titrant solution	5.2.61	X	X		X					

Dissolve 200.0 ± 0.1 g of potassium cyanide (5.1) in 1 L of water (5.2.59).

5.2.40 Potassium dichromate solution

Dissolve 1.6350 ± 0.0001 g of potassium dichromate (5.1) in 900 mL of water (5.2.59). Dilute to the 1 L volumetric mark with water (5.2.59). Calculate the factor of the N/30 dichromate solution from the specified label purity and label accordingly.

5.2.41 Potassium nitrate (powder or crystals)

5.2.42 Potassium standard solution

Dissolve 0.6336 ± 0.0001 g predried potassium chloride (5.2.38) (110°C for 4 h) in 500 mL of water (5.2.59). Dilute to the 1 L volumetric mark with water (5.2.59). Concentration equivalence is 400 mg of K_2O per L.

5.2.43 Silver nitrate solution

Dissolve 20.00 ± 0.01 g of silver nitrate (5.1) in 1 L of water (5.2.59). Store solution in a brown bottle.

5.2.44 Sodium carbonate anhydrous (powder or crystals)

5.2.45 Sodium chloride (powder or crystals)

5.2.46 Sodium diethyldithiocarbamate (DDTC) solution

Prepare solution daily by dissolving 50.00 ± 0.01 g of DDTC (5.1) in 1 L of water (5.2.59).

5.2.47 Sodium diphenylamine sulfonate solution

Dissolve 0.200 ± 0.001 g of sodium diphenylamine sulfonate (5.1) in 90 mL of water (5.2.59). Dilute to the 100 mL volumetric mark with water (5.2.59). Store solution in brown bottle. (Equivalent substitute barium diphenylamine sulfonate).

5.2.48 Sodium hydroxide solution

Dissolve 280.0 ± 0.1 g of sodium hydroxide (5.1) in 1 L of water (5.2.59), cooling solution as necessary.

5.2.49 Sodium peroxide (crystals or powder)

5.2.50 Sodium pyrosulfate (Equivalent substitute potassium pyrosulfate)

5.2.51 Sodium standard solution

5.2.51.1 General

Dissolve 0.3772 ± 0.0001 g of predried sodium chloride (5.2.45) (110°C for 4 h) in 500 mL of water (5.2.59). Dilute to the 1 L volumetric mark with water (5.2.59). Concentration equivalence is 200 mg of Na_2O per L.

5.2.52 Stannous chloride solution

Add 200 mL of hydrochloric acid (5.2.19) to a 1 L volumetric flask. Add slowly 100.0 ± 0.1 g of stannous chloride dihydrate (5.1). Warm solution gently on steam bath. Dilute to the mark with water (5.2.59). Transfer solution to a brown storage containing a few pieces of tin (5.2.56).

5.2.53 Sulphuric acid (p_{20} 1500 kg per m^3)

5.2.54 Sulphuric acid (p_{20} 1500 kg per m^3), diluted 1+1

5.2.55 Sulphuric acid (p_{20} 1500 kg per m^3), diluted 1+9

5.2.56 Tin metal (granular)

5.2.57 Titanium standard solution

5.2.57.1 General

Weigh 0.2000 ± 0.0001 g of titanium oxide (5.1) into a 30 mL platinum crucible (4.2). Add 5.0 ± 0.1 g of sodium pyrosulfate. Fuse mixture at 1050 ± 50°C for 1 h until a clear melt is obtained. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.55) to a 300 mL beaker. Add 50 mL of sulphuric acid (5.2.55) and heat on steam bath to resolubilize. Cool beaker to ambient and transfer quantitatively to 1 L volumetric flask. Dilute to the mark with sulphuric acid (5.2.55). Concentration equivalence is 200 mg of TiO_2 per L.

5.2.57.2 Working stock calibrations standard

Pipette 20 mL of 5.2.57.1 into a 100 mL volumetric flask. Dilute to the mark with sulphuric acid (5.2.55).

5.2.58 Triethanolamine (p_{20} 1130 kg per m^3)

5.2.59 Water

Distilled water or its equivalent shall be used in the preparation of the solutions.

5.2.60 Xylenol orange solution

Dissolve 1.00 ± 0.01 g of xyenol orange (5.1) in 1 L of water (5.2.59).

5.2.61 Zinc titrant solution

Weigh 0.6357 ± 0.0001 g of precleaned zinc metal (5.1) into a 250 mL beaker (Note 4). Add 10 mL of hydrochloric acid (5.2.21) and cover beaker with a watchglass. Add 5 mL of acetic acid (5.2.21) and adjust pH to 6.0 ± 0.2 with ammonia solution (5.2.9). Cool solution to ambient and transfer quantitatively to a 1 L volumetric flask. Dilute to the mark with water (5.2.59).

6.0 SAMPLE PREPARATION

6.1 General

Ash samples shall be prepared in strict accordance with ISO 1171 (Note 5,6,7). Grind the incinerated ash in a agate mortar to pass a 0.063 mm square mesh test sieve. Store samples in an airtight container.

6.2 Loss in Mass Heating

6.2.1 Procedure

Weigh 1.0000 g ± 0.2 mg of ash (6.1) into a tared platinum crucible (4.2). Incinerate sample in furnace (4.1.1) at 815 ± 10°C, until the difference between the results of two final weighings are less than 0.0004 g.

Note 4 To preclean oxidized zinc metal, wash surfaces with hydrochloric acid (5.2.21). Rinse with water (5.2.59) and acetone (5.2.3.). Predry at 110°C for 5 min prior to weighing.

Note 5 Ash samples removed from industrial hearths are considered acceptable provided they are pretreated as described in 6.1.

Note 6 Some samples lose the more volatile constituents, i.e., sodium, when incinerated at conditions outlined in ISO 1171. To avoid risk of losses, samples rich in volatile elements, may be incinerated at 500 ± 10°C. The deviated ash content at this temperature must be noted when reporting results.

Note 7 When some coals are incinerated at the conditions outlined in ISO 1171, it is possible that a significant variation of amounts of sulphur fixation in the ash may occur. The contents of major elements such as SiO_2 or Al_2O_3 can be influenced by the above effect. To avoid risk of this occurring, coals rich in sulphur and lime sould be incinerated at the precautionary conditions described in ISO 1171, very strictly. That is, the thickness of coal layer should be less than 0.15 g/cm^2, the ventilation through the muffle furnace should be such as to give about five air changes per minute and heating rate should be same as that of Brown coal and lignitic coals.

6.2.2 Calculation

The loss in mass on heating, X, as a percentage, is calculated from the formula:

$$X = \frac{(m_o - m_1)}{m_o} \text{ times } 100$$

where m_o = the initial weight of ash (6.2.1) used, g

m_1 = the final weight of ash (6.2.1) remaining in crucible after incineration, g

7.0 PROCEDURE

7.1 General

Analysis must be completed in duplicate on each sample, using the required number of test portions of the ash (6.1).

7.2 Control Blank

A blank consisting of only the chemical reagents will be treated in parallel with the test portion and under identical conditions. The necessary corrections shall then be applied, where applicable.

7.3 Quality Control

A certified reference material (Note 8) will be treated in parallel with the analysis of the test portions and under identical conditions to assess analytical precision.

Note 8 Suitable materials include ES 681-1, NBS 1632a, NBS 1633a, BCS 269, BCS 315, etc.

7.4 Elemental Analysis

7.4.1 Aluminum

Weigh 0.250 ± 0.001 g of ash (6.1) into a 30 mL tared platinum crucible (4.2). Add 15 mL of hydrofluoric acid (5.2.26) and 5 mL of nitric acid (5.2.33). Carefully evaporate solution to 5 mL final volume, without bumping on a hot plate, occasionally stirring solution with a platinum wire. Remove crucible from heat and add 2 mL of sulphuric acid (5.2.54). Gradually reheat

solution until white fumes appear and continue heating at the setting until all the sulphuric acid has evaporated. Add 5.00 ± 0.01 g of sodium pyrosulphate (5.2.50), mix thoroughly and fuse mixture in a furnace (4.1.1) at 1050 ± 50°C for 1 h, until a clear melt is obtained. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.24) to a 200 mL beaker. Add 70 mL of hydrochloric acid (5.2.24) and heat solution slowly on hot plate to resolubilize melt. Add a few drops of nitric acid (5.2.33) and heat solution to boiling for 1 to 2 minutes. Cool solution to ambient and transfer quantitatively into a 250 mL volumetric flask. Dilute to the mark with water (5.2.59).

Pipette 25 mL of this solution into a 100 mL beaker. Add 10 mL of acetic acid (5.2.2) and adjust the pH to 2.9 ± 0.1 with ammonia solution (5.2.9). Transfer quantitatively solution into a 300 mL separatory funnel. Add 20 mL of chloroform (5.2.12), 20 mL of DDTC solution (5.2.46) and shake the separatory funnel for 1 minute, relieving pressure as necessary. Allow the two layers to separate, drain and discard the lower organic layer. In order to collect the chloroform droplets on upper surfaces, add a further 5 mL of chloroform (5.2.12) and reshake the solution for 1 min, relieving pressure as necessary. Allow the two layers to separate, drain and discard the lower layer. Add 2 mL of chloroform (5.2.12) and 10 mL of DDTC solution (5.2.46) to the separatory funnel and shake again for 1 minute, relieving pressure as necessary. Allow the two layers to separate and transfer quantitatively the aqueous layer and separatory funnel washings (5.2.59) into a 300 mL beaker. Pipette the column (V_{11}) of EDTA solution (5.2.15), appropriate to the anticipated per cent by weight of aluminum oxide present in unknown (Table 4), into a 300 mL beaker.

Table 4 - Dilution table (for aluminum)

Al_2O_3 (per cent expected)	EDTA solution (mL to be added)
<30	25
30 - 40	35
>40	1.5 times [Al_2O_3]

Boil the solution for 10 minutes. Remove beaker from hotplate and immediately add 10 mL of ammonia solution (5.2.9). Cool solution to below ambient and adjust the pH to 6.0 ± 0.2 with hydrochloric acid (5.2.24). Add a few drops of xylenol orange solution (5.2.60) and titrate to a pink endpoint with standardized zinc titrant solution (5.2.61). Record volume of titrant used (V_{12}). For calculation and expression of results, see section 8.2.

7.4.2 Calcium

Weigh 0.2500 ± 0.001 g of ash (6.1) into a tared platinum crucible (4.2). Add 5.00 ± 0.01 g of sodium carbonate (5.2.44) and mix thoroughly. Fuse sample at 1050 ± 50°C for at least 40 minutes, until a clear melt is obtained. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.23) into a 500 mL beaker. Add 70 mL of hydrochloric acid (5.2.23), 50 mL of perchloric acid (5.2.36) and heat solution gradually on a hotplate. When white fumes appear, cover beaker with a watchglass and evaporate to dense white fumes of perchloric acid. Maintain this steady refluxing for at least 15 minutes. Cool beaker to ambient and redissolve residue in 50 mL of hydrochloric acid (5.2.23). Filter solution through a medium textured, ashless filter paper (Note 9), collecting filtrate and washings (5.2.25) in a 500 mL beaker and a Residue A.

Wash filter paper and Residue A three times with warm hydrochloric acid (5.2.25), collecting washings in the 500 mL beaker. Rewash Residue A three more times with warm water (5.2.59), collecting washings in the 500 mL beaker. Save Residue A.

Combine filtrate and all washings in a 500 mL beaker, cover beaker with a watchglass and evaporate on hot plate to the appearance of dense white fumes of perchloric acid. Maintain this steady refluxing action for at least 15 minutes. Cool solution to ambient and redissolve precipitated salts in 50 mL of hydrochloric acid (5.2.25). Filter this solution through a medium textured, ashless filter paper recovering Residue B. Wash Residue B three times with warm hydrochloric acid (5.2.25) and warm water (5.2.59), collecting a Filtrate B (which also contains the washings).

Note 9 Insoluble hydrous silica will adhere to the insides of a beaker and will not be removed by spraying with a jet of water. This residue must be scraped off with a rubber policeman.

Combine Residues A and B by placing the filter papers in a tared platinum crucible and incinerate residue at 800 ± 10°C for at least 30 minutes. Cool crucible to ambient, add 2 mL of sulphuric acid (5.2.24) and 5 mL of hydrofluoric acid (5.2.26). Heat slowly at first, then incinerate at 800 ± 10°C for 1 h to vaporize silica and evaporate sulphuric acid. Cool crucible to ambient and add 1.00 ± 0.01 g of sodium pyrosulphate (5.2.50). Mix thoroughly, and fuse mixture at 1050 ± 50°C for at least 1 h until a clear melt is obtained. Cool crucible to ambient, add 15 mL of water (5.2.59) and a few drops of hydrochloric acid (5.2.19) and heat to resolubilize melt (Solution B). Evaporate on a hotplate, Filtrate B to the appearance of dense white fumes of perchloric acid. Cool solution to ambient and dilute to 100 mL volume with water (5.2.59). Combine Solution B and Filtrate B.

To this combined solution, add a few drops of methyl red solution (5.2.32) and adjust the pH to 7.2 ± 0.2 with ammonia (5.2.9). Heat this solution on a hotplate to boiling, then remove and cool to ambient. Quantitatively filter solution, washing precipitate with ammonium chloride solution (5.2.6). Collect filtrate and washings (5.2.6) in a 200 mL beaker (Solution C). Wash (5.2.39) the precipitate off the filter paper into a 300 mL beaker. Add 5 mL of hydrochloric acid (5.2.23) to 300 mL beaker and heat slowly to redissolve precipitates. Cool solution to ambient and add sufficient water (5.2.59) to bring volume to 50 mL. Add a few drops of methyl red solution (5.2.32) and adjust the pH to 7.2 ± 0.2 with ammonia solution (5.2.9). Heat solution on a hotplate to boiling, then remove and cool to ambient. Quantitatively filter solution through an ashless, medium textured filter paper, collecting filtrate. Wash precipitate four times with ammonium chloride solution (5.2.6) collecting washings. Combine filtrate, ammonium chloride washings (5.2.6) and Solution C into a 500 mL beaker and evaporate on a hotplate the solution to a 200 mL final volume. Cool to ambient and quantitatively transfer solution to a 250 mL volumetric flask. Dilute to the mark with water (5.2.59) (Solution D).

Pipette 100 mL of Solution D into a 300 mL beaker and adjust the pH to 13.0 ± 0.5 with sodium hydroxide solution (5.2.48). Pipette 5 mL of potassium cyanide solution (5.2.39) into this solution, mix thoroughly and let stand for at least 5 minutes. Add 0.075 ± 0.025 g of NN indicator (5.2.34) and titrate to a blue endpoint with standardized EDTA solution (5.2.15). Record volume (V_{Ca}) used. For calculation and expression of results, see section 8.3.

7.4.3 Iron

7.4.3.1 General

Weigh 0.2500 ± 0.0001 g of ash (6.1) into a tared platinum crucible (4.2). Add 15 mL of hydrofluoric acid (5.2.26). Carefully evaporate solution on a hotplate without bumping to a final volume of 5 mL, occasionally stirring solution with a platinum wire. Remove from heat and add 2 mL of sulphuric acid (5.2.54). Gradually reheat solution until white fumes appear and continue heating at this setting until all the sulphuric acid has evaporated. Add 5.00 ± 0.01 g of sodium pyrosulphate (5.2.50), mix thoroughly and fuse mixture in a furnace (4.1.1) at 1050 ± 50°C for 1 h until a clear melt is obtained. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.24) into a 200 mL beaker. Add 70 mL to hydrochloric acid (5.2.24) to beaker and heat slowly on a hotplate to resolubilize melt. Add a few drops of nitric acid (5.2.33) and continue heating to boiling for 1 to 2 minutes longer. Cool solution to ambient and add a few drops of methyl red solution (5.2.32). Adjust the pH to 7.2 ± 0.2 with ammonia solution (5.2.9) and then add 1 to 2 drops in excess of ammonia solution (5.2.9). Heat solution on a hotplate to incipient boiling for a few minutes and then cool solution to ambient. Quantitatively filter solution through an ashless, medium textured filter paper, discarding filtrate. Wash precipitate five times with warm ammonium chloride solution (5.2.6), discarding filtrate.

Transfer precipitate off filter paper surfaces into a 250 mL beaker. Replace filter paper into filtering funnel and filter, collecting filtrate, 30 mL of hot hydrochloric acid (5.2.22) through the filter paper to dissolve any remaining precipitate. Quantitatively wash the filter paper at least five more times with hot hydrochloric acid (5.2.22), collecting filtrate (f_1). Finally, wash filter paper with warm ammonium chloride solution (5.2.6) collecting filtrate (f_2) until this filtrate indicates no acid reaction when tested with litmus paper. Discard the cleaned filter paper. Combine filtrates (f_1+f_2) into the 250 mL beaker containing the precipitate and heat to resolubilize. Cool solution to ambient and transfer solution quantitatively into a 250 mL volumetric flask. Dilute to the mark with water (5.2.59).

Pipette 100 mL of this solution into a 500 mL beaker. Add 10 mL of hydrochloric acid (5.2.19) and heat solution with stirring to between 80 and 90°C. Immediately add sufficient stannous chloride solution (5.2.52) dropwise

to the solution until the yellow colour (of ferric chloride) just disappears. Then add one additional drop of stannous chloride solution (5.2.52). Wash down the beaker's inside walls with water (5.2.59), while cooling the solution to below ambient. Add by pipette, 10 mL of mercuric chloride solution (5.2.29), mix thoroughly and let stand for 3 to 5 minutes. Add 30 mL of acid mixture (5.2.5), mix thoroughly and dilute solution to a final volume of 300 mL with water (5.2.59). Add a few drops of sodium diphenylamine sulphonate solution (5.2.47) and titrate to a violet endpoint with standardized potassium dichromate solution (5.2.40). Record titrant volume (V_{21}) used. For calculation and expression of results, see section 8.4.

7.4.3.2 Chemical blank determination

Add 15 mL of hydrofluoric acid (5.2.26) to a tared platinum crucible (4.2). Carefully evaporate solution to a 5 mL volume on a hotplate without bumping, occasionally stirring solution with a platinum wire. Remove crucible from heat and add 2 mL of sulphuric acid (5.2.54). Gradually reheat solution until white fumes appear and continue heating at this setting until all the sulphuric acid has evaporated. Add 5.00 ± 0.01 g of sodium pyrosulphate (5.2.50), mix thoroughly and fuse mixture in a furnace (4.1.1) at 1050 ± 50°C for 1 h until a clear melt is obtained. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.24) into a 200 mL beaker. Add 70 mL of hydrochloric acid (5.2.24) to beaker and heat slowly on a hotplate to resolubilize melt. Add a few drops of nitric acid (5.2.33) and continue heating to boiling for 1 to 2 minutes longer. Cool solution to ambient and transfer quantitatively solution into a 250 mL volumetric flask. Dilute to the mark with water (5.2.59).

Pipette 100 mL of this solution into a 500 mL beaker. Add 10 mL of hydrochloric acid (5.2.19) and heat solution with stirring to between 80 and 90°C. Immediately add sufficient stannous chloride solution (5.2.52) dropwise to the solution until the yellow colour (of ferric chloride) just disappears. Then add one additional drop of stannous chloride solution (5.2.52). Wash down the beaker's inside walls with water (5.2.59) while cooling the solution to below ambient. Add by pipette 10 mL of mercuric chloride solution (5.2.29), mix thoroughly and let stand for 3 to 5 minutes. Add 30 mL of acid mixture (5.2.5), mix thoroughly. Pipette 10 mL of standard ferrous ammonium sulphate solution (5.2.18) into beaker. Dilute solution with water (5.2.59)

to a final volume of 300 mL. Add a few drops of sodium diphenylamine sulphonate solution (5.2.47) and titrate to a violet endpoint with standardized potassium dichromate solution (5.2.40). Record titrant volume (V_{22}) used.

Add 30 mL of acid mixture (5.2.5) into a 500 mL beaker. Pipette 10 mL of standard ferrous ammonium sulphate solution (5.2.18) into beaker, mix thoroughly and let stand for 3 to 5 minutes. Dilute this solution to a final volume of 300 mL with water (5.2.59). Add a few drops of sodium diphenylamine sulphonate solution (5.2.47) and titrate to a violet endpoint with standardized potassium dichromate solution (5.2.40). Record titrant volume (V_{23}) used. The difference between volumes V_{23} and V_{22} will serve as the blank correction volume.

7.4.4 Magnesium

Follow the steps outlined in the preparation procedure for Solution D, as specified in calcium determination (7.4.2).

Pipette 100 mL of Solution D into a 300 mL beaker and adjust the pH to 10.0 ± 0.5 with ammonia solution (5.2.9). Pipette 5 mL of potassium cyanide solution (5.2.39) into this solution, mix thoroughly and let stand for at least 5 minutes. Add a few drops of EBT solution (5.2.16) and titrate to a blue endpoint with standardized EDTA solution (5.2.15). Record volume (V_{mg}) used. For calculations and expression of results, see section 8.5.

7.4.5 Potassium

7.4.5.1 Flame Photometric Method

Weigh 0.2000 ± 0.0001 g of ash (6.1) into a tared platinum dish (4.2). Add 15 mL of hydrochloric acid (5.2.19), 10 mL of hydrofluoric acid (5.2.26) and heat gradually on a hotplate. Add 10 mL of perchloric acid (5.2.36) and increase heat until dense white fumes of perchloric acid are evolved. Evaporate solution until all the hydrofluoric acid is removed. Cool crucible to ambient and add sufficient hydrochloric acid (5.2.20) to redissolve precipitated salts. Quantitatively transfer solution and crucible washings (5.2.20) into a 300 mL separatory funnel. Add 30 mL of methylisobutyl ketone (5.2.30) and shake separatory funnel vigorously for 1 minute, relieving pressure as necessary. Allow the two layers to separate. Draw off and collect the lower aqueous portion into a 200 mL quartz beaker. Add 10 mL of hydrochloric acid (5.2.20) to the separatory funnel and shake vigorously, re-

lieving pressure as necessary. Draw off the lower layer and combine filtrates in the 200 mL quartz beaker. Discard the organic layer remaining in separatory funnel. Heat gently the quartz beaker on a hotplate to evaporate off any organic solvent present. Add 5 mL of nitric acid (5.2.33) and continue heating until the perchloric acid has completely evaporated. Cool solution to ambient, add 5 mL of hydrochloric acid (5.2.21) and reapply heat to resolubilize salts. Add sufficient ammonia solution (5.2.9) to solution to adjust pH to 7.2 ± 0.2. Then add in excess, 5 mL of ammonia solution (5.2.9). Pipette 10 mL ammonium oxalate solution (5.2.7) into solution and boil for at least 3 minutes. Cool solution to ambient and filter through medium textured, filter paper. Transfer filtrate quantitatively into a 100 mL volumetric flask (Solution T).

At optimally adjusted conditions, aspirate the solution into a flame photometer's oxy-hydrogen flame (5.2.35, 5.2.27) and measure the intensity of the emission at a wavelength of 766.5 nanometers. Compare signal intensity to that of the calibration curve's to insure that concentration range limits are adequate. If not, dilute an aliquot of Solution T with water (5.2.59) and repeat measurement.

Calibration curve standards are prepared by pipetting 0,1,2,3 ... 10 mL of potassium standard solution (5.2.42) into a series of platinum crucibles (4.2), each containing 0.0500 ± 0.0001 g of iron (5.1). These working standards are then subjected to an identical acid dissolution - organic separation stepwise procedure, (7.4.5.1) before aspirating solution into a flame photometer. Record emission value and plot a graph relating emission reading to weight of potassium oxide present (m_1). For calculation and expression of results, see section 8.6.

7.4.5.2 Atomic Absorption Spectrophotometric Method

Weigh 0.2000 ± 0.0001 g of ash (6.1) into a tared platinum crucible (4.2). Add 15 mL of hydrochloric acid (5.2.19), 10 mL of hydrofluoric acid (5.2.26) and heat gradually on a hotplate. Add 10 mL of perchloric acid (5.2.36) and evaporate solution to near dryness. Cool crucible to ambient, add 10 mL of perchloric acid (5.2.36), 10 mL of water (5.2.59) and reheat to resolubilize precipitates. Cool crucible to ambient and quantitatively transfer solution (with filtering) into a 100 mL volumetric flask. Dilute to the mark with water (5.2.59) (Solution U).

At optimally adjusted conditions, aspirate the solution into an atomic absorption spectrophotometer's air-acetylene flame (5.2.13, 5.2.4) and measure the intensity of the absorbed light at a wavelength of 766.5 nanometers. Compare signal intensity to that of the calibration curve's to insure that concentration range limits are adequate. If not, dilute an aliquot of Solution U with water (5.2.59) and repeat measurement.

Calibration curve standards are prepared by pipetting 0,1,2,3 ... 10 mL of potassium standard solution (5.2.42) into a series of platinum crucibles (4.2) each containing 0.0500 ± 0.0001 g of iron (5.1). These working standards are then subjected to an identical acid dissolution, stepwise procedure (7.4.5.2), before aspirating solution into an atomic absorption spectrophotometer. Record absorbance value and plot a graph relating absorbance to weight of potassium oxide present (m_1). For calculation and expression of results, see section 8.6.

7.4.6 Silicon

Weigh 0.2500 ± 0.0001 g of ash (6.1) into a tared platinum crucible (4.2). Add 5.00 ± 0.01 g of sodium carbonate (5.2.44) and mix thoroughly. Fuse mixture at 1050 ± 50°C for 1 h until a clear melt is obtained, occasionally swirling mixture. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.23) into a 500 mL beaker. Add 70 mL of hydrochloric acid (5.2.23), 50 mL of perchloric acid (5.2.36) and heat gradually on a hotplate. When white fumes appear, cover beaker with a watchglass and evaporate to dense white fumes of perchloric acid. Maintain this steady refluxing action for at least 15 minutes. Cool beaker to ambient and redissolve residue in 50 mL of hydrochloric acid (5.2.23). Filter solution through a medium textured, ashless filter paper, (Note 9), recovering filtrate and washings (5.2.25) in a 500 mL beaker and a Residue M.

Note 9 Insoluble hydrous silica will adhere to the insides of a beaker and will not be removed by spraying with a jet of water. This residue must be scraped off with a rubber policeman.

Wash Residue M three additional times with warm hydrochloric acid (5.2.25), collecting all washings in the 500 mL beaker. Then rewash with warm water (5.2.59), until the washings show a negative acid reaction with litmus

paper. Combine filtrate and all washings, and evaporate on hotplate to near dryness, (slight fuming). Cover beaker with a watchglass and continue fuming to appearance of dense white fumes of perchloric acid. Maintain this steady refluxing action for at least 15 minutes. Cool beaker to ambient and resolubilize residue in 50 mL of hydrochloric acid (5.2.23). Quantitatively filter solution through a medium textured, ashless filter paper, recovering a Residue N. Wash Residue N three times with warm hydrochloric acid (5.2.25) and then with warm water (5.2.59) until the washings show a negative acid reaction with litmus paper. Finally wash Residue N three additional times wish warm water (5.2.59). Discard filtrate and all washings.

Combine Residues M and N by placing the two filter papers in a tared platinum crucible (4.2). Ignite carefully and then incinerate sample at 1050 ± 50°C for 1 h. Cool crucible in a dessicator to ambient. Record weight. Repeat incineration at 1050 ± 50°C until successive final weighings (W_{31}), do not differ by more than 0.0001 g.

Once a constant weight is obtained, moisten residue with 2 mL of sulphuric acid (5.2.54), 5 mL of hydrofluoric acid (5.2.26) and apply sufficient heat for at least 1 h to vaporize silica and evaporate sulphuric acid. Remove crucible from hotplate and incinerate sample at 1050 ± 50°C for 1 h. Cool crucible in a dessicator to ambient. Record weight. Repeat incineration until successive final weighings (W_{32}), do not differ by more than 0.0002 g. For calculation and expression of results see section 8.7.

7.4.7 Sodium

7.4.7.1 Flame Photometric Method

Follow the steps outlined in the preparation procedure for Solution T, as specified in the potassium determination (7.4.5.1).

At optimally adjusted conditions, aspirate the solution into a flame photometer's oxy-hydrogen flame (5.2.35, 5.2.27) and measure the intensity of the emission at a wavelength of 589.0 nanometers. Compare signal intensity to that of the calibration curve's to insure that concentration range limits are adequate. If not dilute an aliquot of Solution T with water (5.2.59) and repeat measurement.

Calibration curve standards are prepared by pipetting 0,1,2,3 ... 10 mL of sodium standard solution (5.2.51) into a series of platinum crucibles (4.2), each containing 0.0500 ± 0.0001 g of iron (5.1). These working

standards are then subjected to an identical acid dissolution - organic separation, stepwise procedure (7.4.5.1), before aspirating solution into a flame photometer. Record emission value and plot a graph relating emission reading to weight of sodium oxide present (m_1). For calculation and expression of results see section 8.8.

7.4.7.2 Atomic Absorption Spectrophotometric Method

Follow the steps outlined in the preparation procedure for Solution U, as specified in the potassium determination (7.4.5.2).

At optimally adjusted conditions, aspirate the solution into an atomic absorption spectrophotometer's air-acetylene flame, (5.2.13, 5.2.4) and measure the intensity of the absorbed light at a wavelength of 589.0 nanometers. Compare signal intensity to that of the calibration curve's to insure that concentration range limits are adequate. If not, dilute an aliquot of Solution U with water (5.2.59) and repeat measurement.

Calibration curve standards are prepared by pipetting 0,1,2,3 ... 10 mL of sodium standard solution (5.2.51) into a series of platinum crucibles (4.2), each containing 0.0500 ± 0.0001 g of iron (5.1). These working standards are then subjected to an identical acid dissolution, stepwise procedure (7.4.5.2), before aspirating solution into an atomic absorption spectrophotometer. Record absorbance and plot a graph relating absorbance to weight of sodium oxide present (m_1). For calculation and expression of results, see section 8.8.

7.4.8 Sulphur

Weigh 0.2000 ± 0.0001 g of ash (6.1) into a 500 mL beaker. Add 20 mL of hydrochloric acid (5.2.22), cover beaker with a watchglass and boil solution gently on a hotplate for 15 to 20 minutes. Filter hot solution through a medium textured filter paper, collecting filtrate in a 500 mL beaker. Wash residue three times with hot water (5.2.59), collecting washings. Combine filtrate and washings and dilute with water (5.2.59) to a final volume of 150 mL. Add 2 to 3 drops of methyl orange solution (5.2.31) and titrate with ammonia solution (5.2.9) to an orange endpoint. Add 1 mL of hydrochloric acid (5.2.19) to the solution. If any precipitate forms, add dropwise sufficient hydrochloric acid (5.2.19) to resolubilize precipitate. Dilute solution with water (5.2.59) to a final volume of 250 mL. Cover beaker

with watchglass and heat solution with stirring on a hotplate to boiling. Reduce heat until ebullition ceases. With constant stirring, add slowly from a burette, 10.0 mL of warm barium chloride solution (5.2.11) to the vortex of the solution and maintain heating and stirring rate for 30 additional minutes. Cool solution to ambient. Decant supernatant and filter quantitatively, the solution through a medium textured, ashless filter paper. Wash the precipitate with hot water (5.2.59) until the washings do not indicate more than a faint opanescence when tested with silver nitrate solution (5.2.43).

Place the filter paper in a tared covered platinum crucible (4.2). Ignite carefully, remove lid and then incinerate sample at 750 ± 25°C for 1 h. Cool crucible in a dessicator to ambient. Record weight (W_s) (Note 10). For calculation and expression of results, see section 8.9.

Note 10 Add an additional chemical control blank and subtract the mean value W_B of the two from W_s to produce a net weight gained due to sulphur in sample only.

7.4.9 Titanium

Weigh 0.5000 ± 0.0001 g of ash (6.1) into a sintered alumina crucible (4.2). Add 5.00 ± 0.01 g of sodium peroxide (5.2.49) and mix thoroughly. Add an additional 0.50 ± 0.01 g of sodium peroxide (5.2.49) to cover mixture. Heat sample slowly to expel inherent moisture, then fuse at 1050 ± 50°C for 1 h until a clear melt is obtained. Cool crucible to ambient and transfer quantitatively melt and crucible washings (5.2.22) into a 200 mL beaker. Add 40 mL of warm water (5.2.59) and 20 mL of hydrochloric acid (5.2.19) to redissolve melt. Heat this solution on a hotplate to boiling (to decompose the sodium peroxide). If turbidity is present, add a few drops of hydrogen peroxide (5.2.28) and boil for 3 additional minutes. Cool solution to ambient and transfer solution quantitatively into a 200 mL volumetric flask. Dilute to the mark with water (5.2.59) (Solution G).

Pipette an aliquot of Solution G containing an anticipated 10 to 300 micrograms of titanium oxide, into a 50 mL volumetric flask. Add via pipette 8 mL of ascorbic acid (5.2.10) and mix thoroughly. Add via pipette 8 mL of hydrochloric acid (5.2.21) and 20 mL of diantipyrylmethane solution (5.2.14). Dilute to the mark with water (5.2.59), mix thoroughly and let stand for at least 20 minutes.

At optimally adjusted spectrometer conditions, measure the absorbance of the solution in a 10 mm measuring cell at a wavelength of 385.0 nanometers, using a water reference blank to zero instrument. Record absorbance value (V_a) and compare signal intensity to that of the calibration curves to insure that concentration range limits are adequate. If not, dilute an aliquot of Solution G and repeat colorimetric procedure to determine titanium oxide concentration (m_{41}).

Calibration curve standards are prepared by pipetting 0,1,2,3 ... 8 mL of the working stock calibration standard (5.2.57.2) into a series of labelled 50 mL volumetric flasks. Add via pipette 8 mL of ascorbic acid (5.2.10) and mix thoroughly. Add via pipette 8 mL of hydrochloric acid (5.2.21) and 20 mL of diantipyrylmethane solution (5.2.14). Dilute to the mark with water (5.2.59), mix thoroughly and let stand for at least 20 minutes.

At optimally adjusted spectrometer conditions, measure the absorbance of the solution in a 10 mm measuring cell at a wavelength of 385.0 nanometers, using a water reference blank to zero instrument. Record absorbance value and plot a graph relating absorbance to weight of titanium oxide present. For calculation and expression of results, see section 8.10.

8.0 CALCULATION AND EXPRESSION OF RESULTS

8.1 General

The mean calculated concentration between duplicates analyzed using two separate ash portions (6.1), shall be reported on a dry basis, as percentage of oxide in the ash. These results can then be corrected to a dry combustible free basis (Note 11), using the following formula:

$$\begin{matrix}\text{Dry} \\ \text{Combustible free basis} \\ \text{(per cent oxide)}\end{matrix} = \frac{100[\text{oxide per cent}]}{100 - [\text{Loss on mass heating, per cent}]}$$

Note 11 A material balance corrected to a dry, combustible-free basis and including phosphorous oxide (as P_2O_5), should range from 98 to 102 per cent accountability. If not, investigate source of error or omission.

8.2 Aluminum

The aluminum oxide content, as a percentage by mass, is calculated using the formula:

$$\underset{\text{(per cent)}}{Al_2O_3} = \frac{[V_{11}(f)] - V_{12}}{m(L)} \quad 0.051$$

where

V_{11} is the net volume of EDTA solution (5.2.15) used, mL (corrected for chemical blank contributions)

V_{12} is the net volume of zinc titrant solution (5.2.61) used, mL, (corrected for chemical blank contributions).

f is the concentration factor of the standardized 0.01 Molar EDTA solution (5.2.15).

m is the weight of ash (7.4.1) used, g.

L is the dilution factor for the aliquot used.

8.3 Calcium

The calcium oxide content, as a percentage by mass, is calculated using the formula:

$$\underset{\text{(per cent)}}{CaO} = \frac{V_{Ca}\ (f)\ 0.05608}{(m)L}$$

where

V_{Ca} is the net volume of EDTA solution (5.2.15) used, mL, (corrected for chemical blank contributions)

f is the concentration factor of the standardized 0.01 Molar EDTA solution (5.2.15)

m is the weight of ash (7.4.2) used, g

L is the dilution factor for the aliquot used.

8.4 Iron

The ferric oxide content, as percentage by mass, is calculated using the formula:

$$Fe_2O_3 = \frac{V_{21} - (V_{23} - V_{22})}{m(L)} \quad 0.2662$$

where

V_{21} is the volume of potassium dichromate solution (5.2.40) used, mL [for ash used (7.4.3.1)]

$(V_{23} - V_{22})$ is the volume of potassium dichromate solution (5.2.40) used, mL [for chemical blank (7.4.3.2) corrections]

m is the weight of ash (7.4.3) used, g

L is the dilution factor for aliquot used.

8.5 Magnesium

The magnesium oxide content, as a percentage by mass, is calculated using the formula:

$$\underset{\text{(per cent)}}{MgO} = \frac{(V_{Mg} - V_{Ca})\ (f)}{(m)L} \quad 0.04032$$

where

V_{Ca} is the net volume of EDTA solution (5.2.15) used for calcium oxide determination (7.4.2), mL, (corrected for chemical blank contributions)

V_{mg} is the net volume of EDTA solution (5.2.15) used for magnesium oxide determination (7.4.4), mL, [which includes net volume of EDTA (5.2.15) used in calcium oxide determination (7.4.2) and is corrected for chemical blank contributions]

f is the concentration factor of the standardized 0.01 Molar EDTA solution (5.2.15)

m is the weight of ash (7.4.4) used, g

L is the dilution factor for the aliquot used.

8.6 Potassium

The potassium oxide content, as a percentage by mass, is calculated using the formula (for either instrumental techniques):

$$\underset{\text{(per cent)}}{K_2O} = \frac{(m_1)\ 10^{-4}}{m_2}$$

where

m_1 is the net weight of potassium oxide determined in the test portion (7.4.5), mg, (corrected for chemical blank contributions)

m_2 is the weight of ash (7.4.5) used, equivalent to 200 mg, in this case.

8.7 Silicon

The silicon dioxide content, as a percentage by mass, is calculated using the formula:

$$\underset{\text{(per cent)}}{SiO_2} = \frac{(W_{31} - W_{32})\ 100}{m}$$

where

W_{31} is the initial, net weight of residue in crucible after ashing, g (corrected for chemical blank contributions)

W_{32} is the final, net weight of residue in crucible after acid/heat vaporization of W_{31}, g (corrected for chemical blank contributions)

m is the weight of ash (7.4.6) used, g

8.8 Sodium

The sodium oxide content, as a percentage by mass, is calculated using the formula (for either instrumental techniques):

$$\underset{\text{(per cent)}}{Na_2O} = \frac{(m_1)\ 10^{-4}}{m}$$

where

m_1 is the net weight of sodium oxide determined in the test portion (7.4.7), mg (corrected for chemical blank contributions)

m_2 is the weight of ash (7.4.7) used, equivalent to 200 mg in this case.

8.9 Sulphur

The sulphur trioxide content, as a percentage by mass, is calculated using the formula:

$$\underset{\text{(per cent)}}{SO_3} = \frac{(W_s - W_B)\ 34.30}{m}$$

where

W_s is the weight of the precipitate deposited due to test portion, g

W_B is the mean weight of the precipitate deposited due to chemical blank contributions, g

m is the weight of ash (7.4.8) used, g

8.10 Titanium

The titanium oxide content, as a percentage by mass, is calculated using the formula:

$$\underset{\text{(per cent)}}{TiO_2} = \frac{(m_{41})\ 10^{-4}}{m_{42}(L)}$$

where

m_{41} is the net weight of titanium oxide in the aliquot used, mg (corrected for chemical blank contributions)

m_{42} is the weight of ash (7.4.2) used, mg

L is the dilution factor for the aliquot used

9.0 PRECISION

9.1 General

The elemental analysis of the ash sample shall be deemed acceptable when Table 5 range limits are applicable and the corresponding elemental analysis of the certified reference material used [as quality control, (7.3)] agrees with the limits of the repeatability and reproducibility limits set in Table 5.

9.2 Repeatability (r)

The difference between two single results on equivalent test portions by one analyst using the same apparatus within a short time interval, shall not exceed the repeatability limit (r) more than once (1) in twenty (20) cases in the normal and correct operation of the method. When such a difference is found to exceed the repeatability limit (r), there is reason to suspect one or both of the results.

i.e. Duplicate analysis for siliceous dioxide are 60.10% and 61.20%. The repeatability (r) from Table 5 is 1.3%. The absolute difference between the two results is 1.1%. Since the absolute difference does not exceed r, the analysis are considered acceptable at the 95 per cent confidence level.

9.3 Reproducibility (R)

The difference between two single and independent results determined by two analysts working in different laboratories on equivalent test portions shall not exceed the reproducibility limit (R) more than (1) in twenty (20) cases in the normal and correct operation of the method. When such a difference is found to exceed the reproducibility limit (R), there is reason to suspect one or both of the results.

Table 5 - Precision limits (Note 12)

Element as oxide	Applicable range wt % as oxide	Repeatability r	Reproducibility R
Al_2O_3	12 - 30	0.55	1.50
CaO	1.0 - 18	0.30	0.65
Fe_2O_3	2.0 - 40	0.99	2.20
MgO	0.4 - 4.5	0.16	0.88
K_2O	0.2 - 2.0	0.14	0.33
SiO_2	30 - 65	1.30	1.70
Na_2O	0.1 - 3.0	0.21	0.44
SO_3	1.0 - 16	0.22	0.52
TiO_2	0.5 - 2.0	0.07	0.56

10.0 ANALYSIS REPORT

The report analysis shall include:

i) a sample identification number (cross referenced, if necessary);

ii) a reference to method of analysis (and any deviations, if applicable);

iii) results expressed on a dry basis (as a percentage oxide) and/or on a dry combustible free basis (as a percentage oxide).

Note 12 Calculated employing ISO 5725 from data supplied by six laboratories on three different, yet equivalent test samples.

POOR

QUALITY

ORIGINAL